

An on-the-fly approach optimized switching: A special case of free energy simulation under nonequilibrium feedback control

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We discuss the optimized switching free energy simulations in an analogy with the systems which are driven under nonequilibrium feedback control. We find an on-the-fly simulation approach of switching optimization is a special case of the nonequilibrium process under feedback control. In this approach, the switching rate is allowed to vary during the simulation and the optimization is done on-the-fly by utilizing the part of the simulation outcomes as the feedback information. In such a case, one should use generalized Jarzynski equality under nonequilibrium feedback control for free energy calculation instead original Jarzynski equality.

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There are very few relations in statistical dynamics has been used to calculate the equilibrium thermodynamics properties for the systems which are driven arbitrarily far-from-equilibrium [1–3]. One of these is the Jarzynski equality [1] which relates nonequilibrium measurements of the work done on the system to equilibrium free energy differences. The second law of thermodynamics can be quantitatively described by the fluctuation theorem which are closely related to the Jarzynski equality [1, 2]. A system initially at equilibrium with temperature (inverse) $\beta = 1/k_B T$ is externally driven from its initial state to final state by nonequilibrium process satisfies the detailed fluctuation theorem,

$$\frac{P(W)}{P(-W)} = e^{\beta(W-\Delta F)} \quad (1)$$

and its integrated version, the Jarzynski equality

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}. \quad (2)$$

Where W denotes the work performed on the system, ΔF is the free energy difference of the system between its final and initial equilibrium states and $P(\pm W)$ is the work probability distribution in forward (+) and reverse (-) direction. This relationship is widely used in experiments [4, 5] as well as simulations [6] in many branches of Science (see, eg.[7]).

Various experiments and simulations has been performed by adopting a suitable time-dependent driving scheme described by an external control switching protocol. Even though the Jarzynski equality is valid for any time-dependent driving scheme, the efficiency of a nonequilibrium switching simulation which use Jarzynski equality to estimate precise free energy difference is depends on the switching function. A well selected

switching function can significantly minimize the associated dissipated work $W_d = W - \Delta F$ and reduce the computational cost of nonequilibrium free energy simulation [8–10].

In simulations, one has to search for the switching protocol that minimizes the mean work required to drive the system from one given equilibrium state to another in finite time such that the exponential average should provides precise free energy estimates [8–10]. Since the optimized switching protocol minimizes the average work [10], most nonequilibrium free energy simulations which use Jarzynski equality employ optimized switching function [11]. One simple and reasonable method of optimization utilizes the informations obtained from an ensemble of short simulation which are carried out at relatively low switching speeds, usually within the linear response regime [11]. Once the optimized control switching parameter has been estimated, the long run free energy simulations then performed with the optimized switching function at a slower speed.

In a recent paper [12], an on-the-fly approach is proposed for estimating an efficient switching function during a single nonequilibrium free energy simulation. In this approach, the part of the simulation carried out by allowing the switching function to vary and the remaining part continued with the optimized switching function which has been estimated on-the-fly. In this approach, the informations obtained from the earlier part of the simulation outcomes are used to estimate the optimized switching function. Here, the informations used for optimization are the switching rate, the variance of the simulation outcomes and its autocorrelation function [11, 12]. It has been shown very recently that the accuracy of the free energy estimates also depends on shape of the switching protocol [13].

In most of the optimization problems [11–13], the (feedback) informations about the physical system plays crucial role in a direct or indirect way to calculate the optimized switching functions. This can provide the natural

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link between the switching optimization and the informations. In this paper, we discuss the optimized switching free energy simulations in an analogy with the systems which are driven under nonequilibrium feedback control [14] and argue that the work value obtained from an on-the-fly approach in general does not satisfy Jarzynski equality.

The evolution of the physical systems can be modified or controlled by repeated operation of an external agent called controller [14, 15]. In contrast to open loop controller which operates on the system blindly, the feedback or closed loop controllers use information about the state of the system. The feedback is the process performed by the controller of measuring the system, deciding on the action given the measurement output, and acting on the system [16]. For example, in a single molecule Atomic Force Microscopy experiment, the external agent is an electric feedback circuit which detects the motion of the cantilever and manipulate the control force proportional to its velocity [17]. The proper utilization of the information about the state of the system in feedback control effectively improves the system performance [14–18]. However, the presence of feedback control in physical system modifies both the Jarzynski equality and the fluctuation theorem [17].

Recently, the Jarzynski equality is generalized to an experimental condition in which the system is driven between two equilibrium state via nonequilibrium process under forward feedback control [19]. At a given time, the controller measure the partial state of the system. The result of the measurement determines the action the control will take. The additional information on the system provided by the measurement further determines the system states. The equilibrium free energy difference for the driven system (which locally satisfies detailed fluctuation theorem) under nonequilibrium feedback control can be calculated from the generalized Jarzynski equality [19]

$$\langle e^{-\sigma-I} \rangle = 1, \quad (3)$$

where $\sigma = \beta(W - \Delta F)$ and I is the mutual information measure obtained from the feedback controller [19]. The average is taken from the distribution of work in forward direction with feedback control. The work distribution with feedback control is computed without the knowledge of internal details of the controller [19].

Let $P(W, I) = P(W|I)P(I)$ be the (joint) probability distribution of work with feedback information. The above equality, Eq.(3), can be written as,

$$\int \int P(W|I)P(I) e^{-\sigma-I} dW dI = 1, \quad (4)$$

where $P(W|I)$ is the conditional probability for obtaining the outcome W given the mutual information measure I . Since the controller often measure the partial state of the system, the changes in feedback information measure [16, 20] occurs with probability $P(I)$.

The feedback control enhances our controllability of small thermodynamics systems [14–18]. In free energy simulations this feedback mechanism can be very helpful for sampling rare trajectories for precise free energy difference calculations. Since the work that performed on a thermodynamic system can be lowered by feedback control [18, 19], we can say that using proper feedback mechanism in a free energy simulation is equivalent to carry out an optimized switching free energy simulation which minimizes the average work. In this perspective, we notice that an on-the-fly approach is a special case of nonequilibrium process under feedback control as follows.

In simulations, the free energy difference between the two equilibrium states can be calculated in general by pulling the sytem from one equilibrium state to another state along a switching path. The path connecting the two states will be parameterized using the variable λ , with $0 \leq \lambda \leq 1$. The switching rate describes the nature of the switching process to be an equilibrium (infinitely slow) or nonequilibrium (fast). In an on-the-fly approach, up to the history length time, t_h [12], the switching function parameter, λ_t , vary during the simulation. The simulation outcomes obtained within t_h are used as a feedback information to estimate the optimized switching function, λ_t^* . The remaining part of the simulation carried out with this fixed λ_t^* . This is equivalent to say, at time t_h , the (un-known) controller [23] measure the partial state of the system and determines the optimized switching function λ_t^* . Once the switching function to be optimized, the outcome of the remaining part (after t_h) of the simulation is performed by fixed feedback control with feedback information measure, $I(\lambda_t^*)$.

In this aspect, the feedback information in an on-the-fly approach can be characterized by the mutual information measure [19], $I_1 = 0$ for $t \leq t_h$ and $I_2 = I(\lambda_t^*)$ for $t > t_h$. From a single measurement of the controller, at t_h the mutual information measure $I(\lambda_t^*)$ is obtained over all simulation outcomes for $t \leq t_h$. The term mutual information is appropriate in the sense that in this approach, the optimized switching function λ_t^* depends on the feedback information measure $I(\lambda_t^*)$ which in turn depends on λ_t^* for further simulation. In an on-the-fly approach, the switching function is fixed at λ_t^* after t_h which indicates that the controller measure the partial state of the system only once (at t_h) for system control (switching optimization) instead of many times in general. In this sense, we can say that an on-the-fly approach is a special case of nonequilibrium process under feedback control.

It should be noted that, in systems with feedback control the simulation/experimental outcomes are different from controller measurement outcomes. A single outcome of the controller measurement is a result of analyzing many realizations of the simulation/experimental outcomes. That is the controller utilizes the part of the simulation/experimental outputs and calculate its

measurement outcome, see ref.[15]. In an on-the-fly approach, the controller utilizes all simulation outcomes for $t \leq t_h$ and obtained the optimized switching function λ_t^* . Due to the single measurement of the controller at t_h , work outcomes of the simulation associated with mutual information measure $I_1 = 0$ for $t \leq t_h$ and $I_2 = I(\lambda_t^*)$ for $t > t_h$. Since the equality, Eq.(3), does not depends on the internal details of the controller [16, 19] and the controller made measurement only once at $t = t_h$, Eq.(4) can be written in this case as

$$\gamma(I_1) P(I_1) + \gamma(I_2) e^{-I_2} P(I_2) = 1, \quad (5)$$

where,

$$\gamma(I_i) = \int P(W|I_i) e^{-\sigma} dW, \quad (i = 1, 2). \quad (6)$$

In contrast to the original Jarzynski equality, $\langle e^{-\sigma} \rangle = 1$, if we measure $\langle e^{-\sigma} \rangle$ in the presence of the feedback control, the calculated value is differ from unity [19] which is given as

$$\langle e^{-\sigma} \rangle = \gamma, \quad (7)$$

where γ is a measure which characterizes the efficacy of the feedback control [19]. Hence, in an on-the-fly approach, the free energy difference obtained from original Jarzynski equality [12] is in general inappropriate. In this approach one should use the generalized Jarzynski equality with proper feedback information measure $I(\lambda_t^*)$ provided the simulation process should satisfy the local detailed balance or the detailed fluctuation theorem [19].

Since the switching function under feedback control depends on the controller measurement outcomes [19], if we perform nonequilibrium simulation under feedback control, the different trajectories will have different switching function. These kind of different switching function has been incorporated in an on-the-fly approach simulation [12] clearly confirm that this approach is a special case of free energy simulation with feedback control. Thus, the work value obtained from an on-the-fly approach in general does not satisfy original Jarzynski equality. The un-noticed sign of violation of original Jarzynski equality for those simple systems studied in an on-the-fly approach [12] is in question. In fact, the free-energy estimate by the original Jarzynski equality for those systems studied in an on-the-fly approach seems to be pretty good which can makes a general impression that the generalized Jarzynski equality does not needed. The main motivation for our analogy argument of on-the-fly approach with nonequilibrium process under feedback control is that the stated conclusion of the un-noticed sign of violation of original Jarzynski identity in an on-the-fly approach is not definite for all systems (see, ref. [17]), particularly, the folding and unfolding free energy simulations studies for complex macromolecular systems. It would be interesting to carry such an investigation on

macromolecular systems which has many folding intermediates [21]. Finally, If one can carry on-the-fly approach simulation studies on complex systems and insist to use original Jarzynski equality for free energy estimates, within the confident level of certain hypothesis [22] one should properly test the violation of original Jarzynski equality.

In conclusion, our analogy argument of the switching optimization with nonequilibrium process under feedback control indicates that an on-the-fly approach switching simulation is a special case of a nonequilibrium free energy simulation with feedback control. In such a case, using generalized Jarzynski equality under nonequilibrium feedback control is appropriate for free energy difference calculation instead original Jarzynski equality.

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